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# TECHNICAL NOTE

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## SPECTRALLY SELECTIVE PHOTODETECTORS FOR THE MIDDLE AND VACUUM ULTRAVIOLET

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## **SUMMARY**

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A number of "solar blind" photodetectors have been developed in recent years. Measurements made on several phototubes with photocathodes of rubidium-tellurium, cesium-tellurium, cesium-iodine and copper-iodine are described. Cathode quantum efficiencies for semi-transparent cathodes of rubidium-tellurium or cesium-tellurium range from  $10^{-1}$  to  $10^{-2}$  photoelectrons/quantum in the middle and vacuum ultraviolet, with long wavelength responses of less than  $10^{-4}$  photoelectrons/quantum beyond about 3500Å. By combining solar blind cathodes with windows of LiF, CaF<sub>2</sub>, or fused silica, detectors with relatively flat quantum efficiencies can be produced, marked by high sensitivities in specific ultraviolet spectral regions and by very low sensitivities at all longer wavelengths.

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## INTRODUCTION

The need for photodetectors that are efficient in the middle and vacuum ultraviolet but relatively insensitive in the near ultraviolet and visible has led, in recent years, to the development of a variety of spectrally selective ultraviolet photodetectors (References 1 and 2). The photoemissive surfaces in these devices have been described as "solar blind" (Reference 3). This term refers to the fact that these detectors are relatively insensitive to wavelengths greater than about 3000Å and thus quite unresponsive to solar radiation viewed through the earth's atmosphere. Photocathodes with these solar blind responses are very useful for astrophysical and geophysical experiments in the ultraviolet, as well as for laboratory ultraviolet spectroscopy or radiometry wherever the amount of long wavelength stray light is undesirably large. The "middle" ultraviolet is considered to extend from 3000Å to 2000Å, with the "far" or "vacuum" ultraviolet extending downward from 2000Å. This report describes the recent program of Goddard Space Flight Center in developing solar blind photodetectors. Future improvements in ultraviolet detectors and answers to questions concerning the physics of high-work function cathodes and their use in phototubes may be anticipated.

Spectrally selective ultraviolet photoemitting surfaces may be of two types: pure metal cathodes such as nickel, tungsten, gold, etc., or composite surfaces such as the well known cesium-antimony (Cs-Sb) or the selective alkali-tellurium surfaces. Pure metal photosurfaces, selective for the middle ultraviolet, have been reported in the literature since the 1920's and an excellent review of these researches in photoelectric emission from solids, emphasizing the vacuum ultraviolet, is contained in a chapter by Weissler in Reference 4. A recent study of gold cathode photomultipliers was made by Childs (Reference 5). Pure metal photosurfaces are characterized by low quantum efficiencies in the middle ultraviolet ( $10^{-3}$  to  $10^{-5}$  photoelectrons/quantum), although the yield of some metals, such as tungsten, may rise to as much as  $10^{-1}$  photoelectrons/quantum at shorter wavelengths in the vacuum ultraviolet (References 4, 5, and 6). Two examples of metal photoemitters will be discussed shortly, in connection with Figure 5.

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Composite photosurfaces of Cs-Sb, Na-K-Cs-Sb, Cs-Sb-O, and Rb-Ag-O have been in use in commercial phototubes for many years (References 7 and 8). The high-yield ultraviolet selective photocathodes of cesium-tellurium (Cs-Te) and rubidium-tellurium (Rb-Te) were reported in 1953 by Taft and Apker (Reference 9) and were further described in 1956 by Harper and Choyke (Reference 10). Since then others have prepared alkali-tellurium opaque and semitransparent photosurfaces (References 11 through 14 and private communications from J. E. Roderick, G. G. Kretschmar, S. Essig, H. L. Sowers, B. Linden, A. H. Sommer, and J. P. Causse). The photoemissive properties of some of these cathodes were studied at the Naval Research Laboratory in the 1950's, and of others, more recently, at Goddard Space Flight Center.

## PHOTODETECTOR RESPONSES

Figure 1 gives the spectral response (quantum efficiency) from 3500A to 1000A of several phototubes containing a variety of representative photocathode materials. The curve marked 1P21 shows the short wavelength portion of the response of this well known Cs-Sb photomultiplier. This tube has

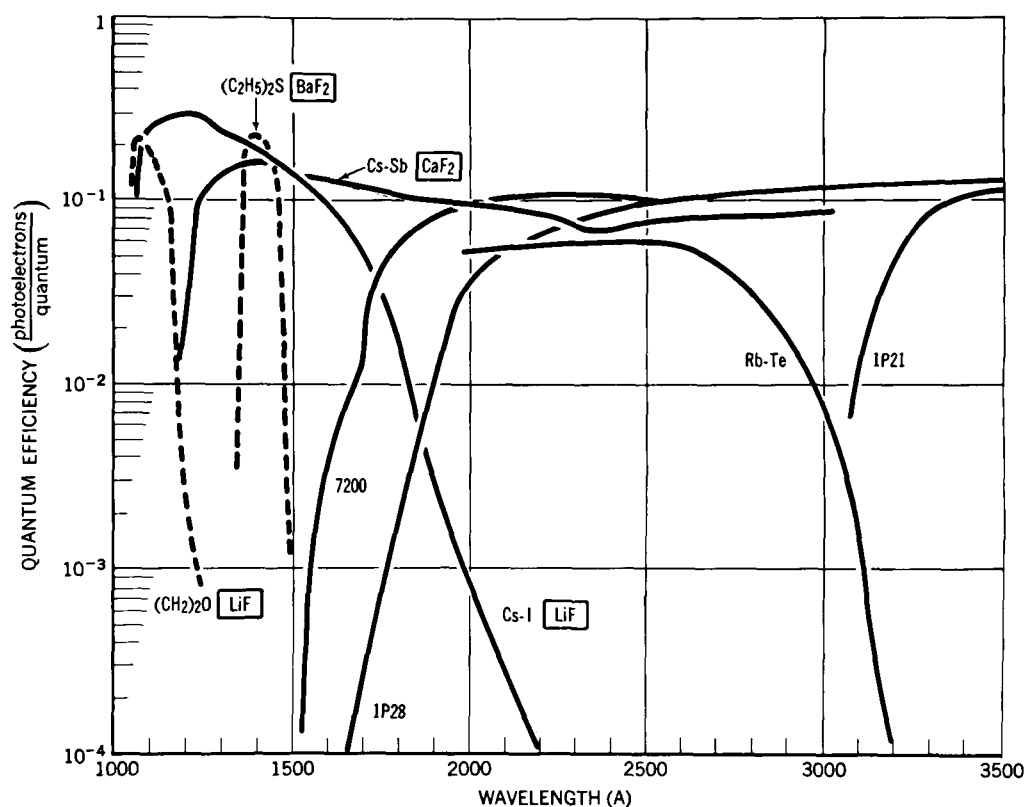


Figure 1—Spectral response curves for representative ultraviolet photodetectors. Boxed symbols refer to the phototube window materials. The 1P21, 1P28, and 7200 curves show the short wavelength portions of photomultipliers with Cs-Sb cathodes and envelopes of glass, Corning 9741 and fused silica, respectively (Reference 15). For comparison, the two dashed curves represent the narrow responses of photoionization chambers containing ethyl sulfide and ethylene oxide (Reference 16).

a glass envelope and is used primarily in the visible region. The 1P28 photomultiplier, introduced some 15 years ago, has an envelope of Corning 9741 ultraviolet transmitting glass which extends the Cs-Sb range by over 1000A, putting it into the beginning of the vacuum ultraviolet as shown. By using a quartz envelope Cs-Sb photosurface, which was described by Dunkelman and Lock (Reference 15), the range is extended to approximately 1600A. A photomultiplier using these materials became commercially available several years ago as type 7200. Recently a photosurface of Cs-Sb with a  $\text{CaF}_2$  window was examined at Goddard Space Flight Center. Figure 1 shows the further extension of the comparatively flat, high quantum efficiency of Cs-Sb down to 1225A with this phototube.

In cases where high efficiencies and solar blindness are desired, one of the alkali-tellurium photosurfaces such as Rb-Te is required. If it is important to limit the response of a photodetector to the vacuum ultraviolet, then a material such as cesium-iodine (Cs-I) with a window of LiF is necessary. Cesium-iodine rejects even more of the middle and near ultraviolet as well as the visible wavelengths. Both of these photocathode materials will be discussed here.

Finally, in Figure 1 there are shown for comparison two dashed lines (ethyl sulfide gas in a chamber with a  $\text{BaF}_2$  window and ethylene oxide gas in an ion chamber with a LiF window) representing examples of relatively narrow response photodetectors which operate not by photoelectric emission from a solid photocathode, as in the above materials, but by photoionization of a gas chamber (Reference 16). Photoionization chambers, with their very narrow vacuum ultraviolet response bands and high quantum efficiencies, have proved useful in vacuum ultraviolet spectroscopy and stellar astronomy from rockets (References 17 and 18).

Figures 2, 3 and 4 give details of the spectral response of several types of spectrally selective solar blind photocathodes. In Figure 2 the responses of several Rb-Te opaque-cathode phototubes are shown. Curves 4 and 5 represent the average of the extremes of many tubes prepared by Roderick (private communication). These curves with their high efficiencies below 2500A may be compared with curves 1 and 2 which show the response of two photodiodes prepared by Kretschmar (private communications and Reference 11). Although exhibiting lower efficiencies, the latter phototubes provide higher selectivity. Curve 1, for example, refers to a photodiode having a quantum efficiency of  $7 \times 10^{-2}$  photoelectrons/quantum at the 2537A mercury line and a rejection ratio of 1000 over the wavelength interval 2900A to 3300A. Curve 3, although representing another photodiode by Kretschmar, is similar to curves 4 and 5 and indicates the variability found in these experimental tubes.

It should be mentioned that no major differences between Rb-Te and Cs-Te cathodes with respect to either quantum efficiency or rejection ratios have been found. Even though some problems are caused by a reaction of the cesium with AgCl seals, most manufacturers have preferred to work with Cs-Te rather than Rb-Te. This choice is evidently based on the desirability of being able to cesiate photomultiplier dynodes to a limited extent, on the ready availability of pure cesium compounds, and on prior familiarity with evaporation of cesium compounds.

In Figure 3 there are compared a variety of Cs-Te cathodes. The curves marked XCD-12 and FW 140-12 show the spectral response of sapphire windowed opaque photodiodes made at the ITT

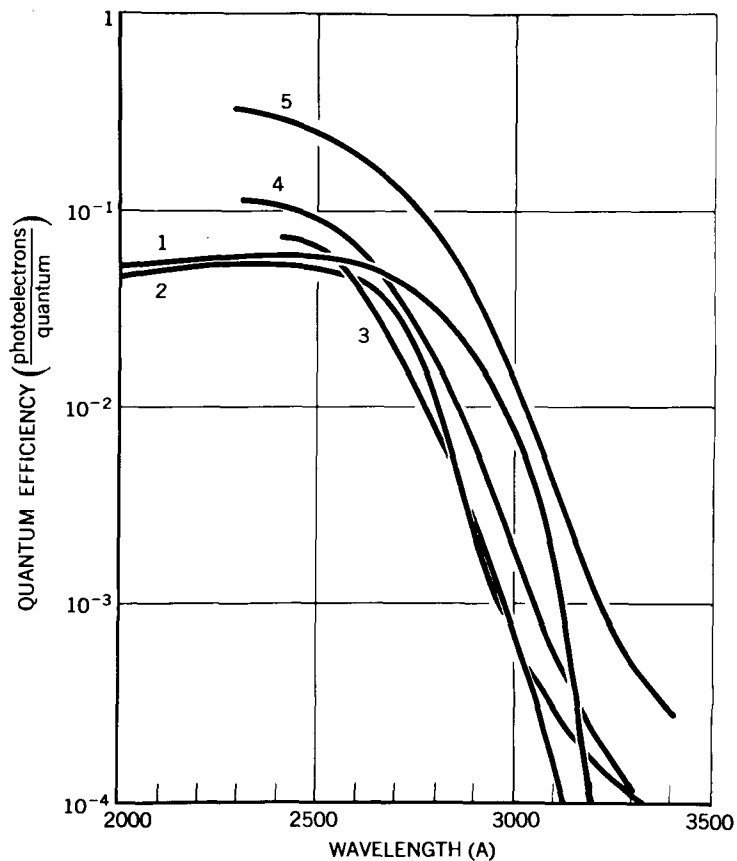


Figure 2—Spectral response curves of Rb-Te opaque-cathode photodiodes showing various degrees of solar blindness and quantum efficiency. Curves 1, 2, and 3 refer to Kretschmar's diodes 16, 4, and 59 (Reference 11 and private communication). Curves 4 and 5 represent Roderick's diodes 21 and 14 (private communication).

Federal Laboratories\*, while the curve marked FW 157-1 refers to an ITT photodiode with fused silica windows. The curve marked S.883 refers to the opaque cathode of a 13-stage photomultiplier with LiF window made by Sommer (Reference 13). Note that a quantum efficiency of better than  $10^{-1}$  photoelectrons/quantum is achieved with these opaque cathodes; the yields are considerably lower on the two lower curves marked 151 and 152, which refer to the response of semitransparent photocathodes in a 14-stage ASCOP† photomultiplier (Causse, private communication). It is not clear with the limited data on hand whether this is due to a transmission loss in the metallic conducting substrate or to incomplete escape of photoelectrons from a thick transmission photocathode. A semitransparent cathode just behind the front window does result in far better optical coupling than is possible in recessed opaque cathodes. This is frequently an important consideration in application.

Figure 4 displays the spectral responses of several high-work function photocathodes. Curve 6 refers to the response of a Cs-I surface from the work of Philipp and Taft (Reference 19) who studied

\*International Telephone and Telegraph Federal Laboratories.

†ASCOP Division of Electro-Mechanical Research, Inc.

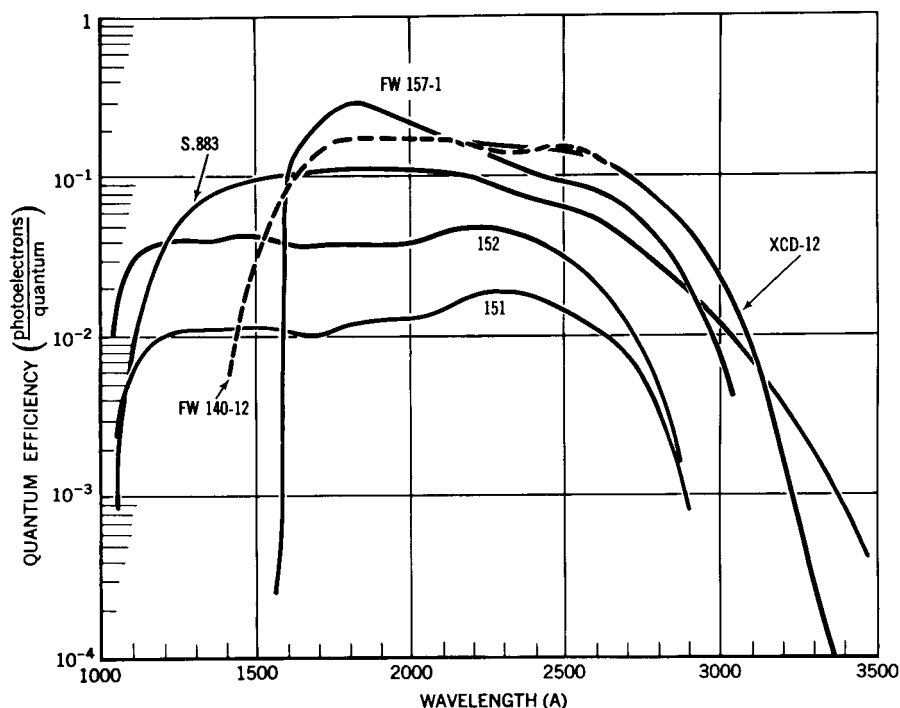


Figure 3—Spectral response curves of Cs-Te phototubes. Note the variation in long wavelength responses as well as the differences in quantum efficiency between opaque and semitransparent cathodes. The FW 140-12 and XCD-12 curves refer to opaque-cathode photodiodes made by the ITT Federal Laboratories with sapphire windows; the FW 157-1 curve is the response of an ITT opaque-cathode diode with a fused silica window; the S.883 curve is the response of a 13-stage photomultiplier with an opaque cathode and LiF window made by Sommer (Reference 13). The 151 and 152 curves represent the responses of 14-stage semitransparent-cathode photomultipliers with LiF windows made at ASCOP (Causse, private communication).

various iodine compounds evaporated on opaque metallic discs. Curve 3 represents recent measurements of the spectral distribution of efficiency from a Cs-I surface prepared by Sommer and studied at Goddard Space Flight Center. Here the photocathode is deposited on a conducting substrate of thin tungsten immediately behind the LiF window which makes possible, again, convenient end-on coupling. Curves 1, 2, and 5 (K-Br, Cs-Br, and Rb-I) are taken from the work of Taft and Philipp (Reference 20) and are shown here for comparison and for a suggestion of surfaces which should be considered if shorter wavelength cutoffs are of interest. The copper-iodine (Cu-I) curve, curve 4, is taken from the work by Shuba and Smirnova (Reference 21) and will be discussed in connection with Figure 5.

The long wavelength response of some of these photocathodes is displayed in Figure 5, where 9 orders of magnitude of quantum efficiency are shown. Curve 1 is the familiar Cs-Sb photosurface discussed in Figure 1. Curve 2 is the Sommer Cs-I surface discussed in Figure 4, but in this figure it can be seen that at 2537 Å the absolute quantum efficiency is only  $7 \times 10^{-6}$  photoelectrons/quantum; this was measured with a calibrated low-pressure mercury arc. Curve 3 is a result of some recent measurements at Goddard Space Flight Center of a Cu-I semitransparent surface on a tungsten substrate in a photodiode made by Sommer. This response is similar to that of his Cs-I tube (curve 2),



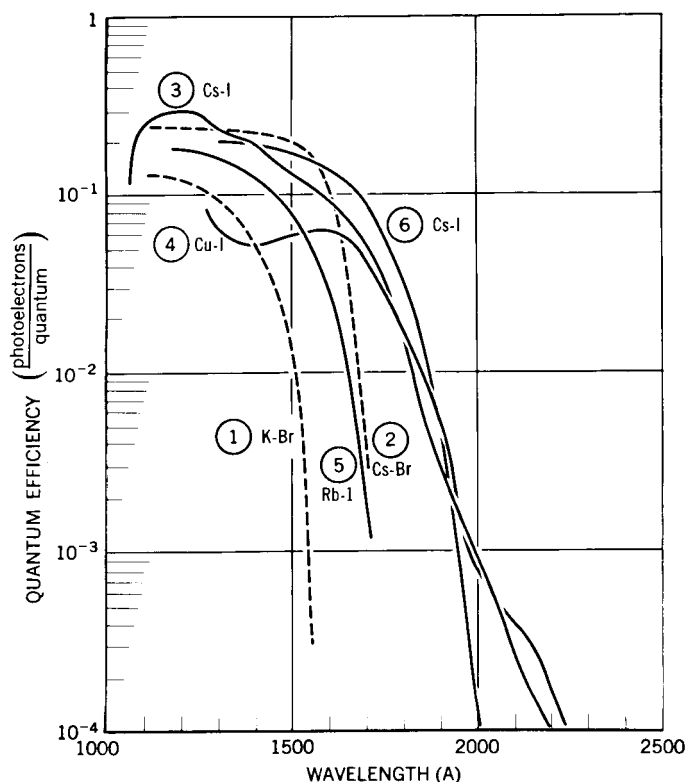


Figure 4—Spectral response curves of several high-work function cathodes. Curve 1, K-Br; curve 2, Cs-Br; and curve 5, Rb-I are taken from the work of Taft and Philipp (Reference 20). Curve 3 is the response of a diode with a semi-transparent cathode of Cs-I behind a LiF window in a tube made by Sommer (Reference 13). Curve 4 is the response of Cu-I estimated from the work of Shuba and Smirnova (Reference 12). Curve 6, the response of Cs-I, is from the paper of Philipp and Taft (Reference 19).

except for the much improved long wavelength rejection ratio which is at least 7 orders of magnitude between 1849Å and 2537Å. The upper limit of yield at the latter wavelength was determined to be less than  $10^{-9}$  photoelectrons/quantum. In both curves 2 and 3 the response has been measured at many wavelengths from about 2000Å down to 1050Å and also at the intense mercury 2537Å line.\* Between 2000Å and 2537Å an estimated curve has been drawn. These measurements can be compared with the results reported in 1960 by Shuba and Smirnova and mentioned in connection with Figure 4. They have estimated a quantum efficiency of  $10^{-1}$  photoelectrons/quantum at the short wavelengths but a rejection ratio of only 6 orders of magnitude. The absolute quantum efficiency of their photo-surface has been estimated from their paper, and curve 4 (Figure 4) is for comparison purposes only. Since their article was published, other yield curves of vacuum ultraviolet photo-emitters have appeared by Tyutikov and Shuba (Reference 22), and Shuba, Tyutikov and Sorokin (Reference 23). In 1957, D. W. Turner of Imperial College reported (Reference 24) a Cu-I photoemitter with a "cutoff" at 2300Å and a peak efficiency somewhere between  $10^{-2}$  and 1 photoelectrons/quantum; however, he does not define "cutoff."

Copper-iodine, it can be seen from Figures 4 and 5, makes a useful detector for spectroscopic studies in the vacuum ultraviolet, not only because of high quantum efficiency but also because it makes negligible the effect of scattered light. This scattered light comes primarily from the longer wavelength emission of the hydrogen or other gaseous discharge tubes generally used with vacuum monochromators. It is also interesting to compare the alkali-iodine surfaces with some of the pure metal photosurfaces. Curves 4 and 4a of Figure 5 show a nickel cathode response which was obtained by combining middle and vacuum ultraviolet measurements made in 1953 as shown in the figure (Reference 6). Copper-iodine appears to be more advantageous at these wavelengths than nickel and other metal photocathodes which have been the only readily available vacuum ultraviolet photoemitters. Finally, we can compare the Cu-I efficiency with that of tungsten, curve 5.

\*The large quantum efficiencies shown for these tubes represents an early and preliminary measurement. Subsequent measurements of Cs-I and Cu-I cathodes show that in general a peak quantum efficiency of 10 to 20 percent is more typical with Cs-I being 3 to 5 times more sensitive than Cu-I at the Lyman-alpha wavelength (1216Å).

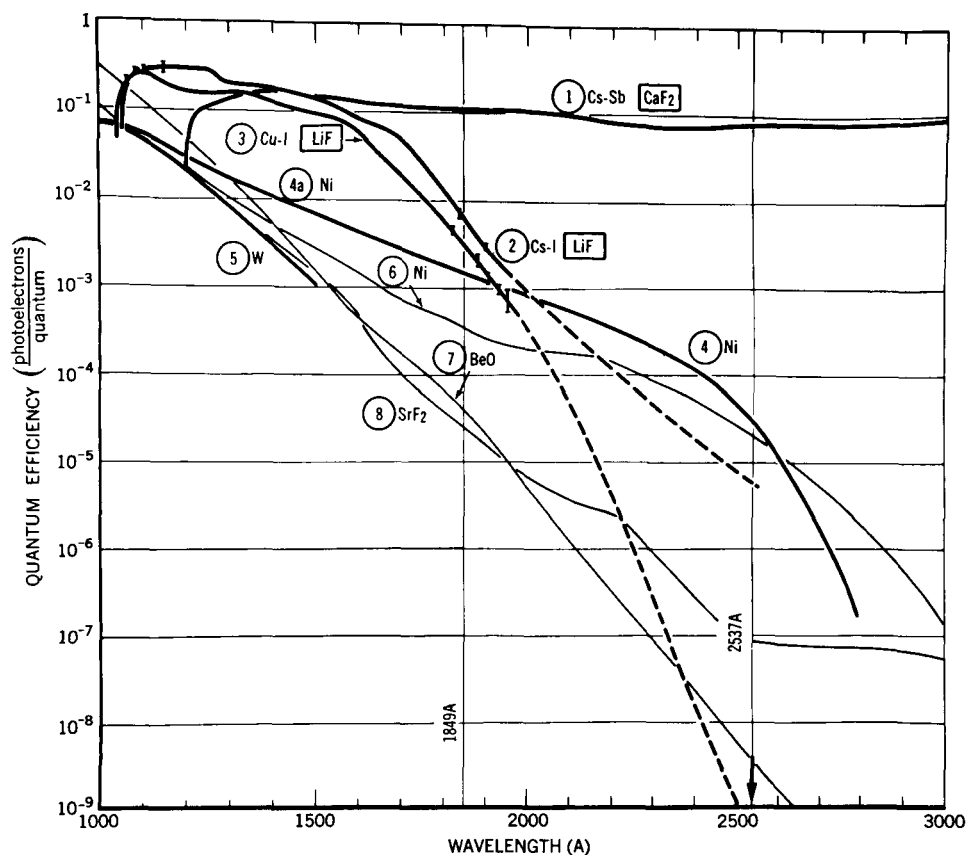


Figure 5—Spectral response curves of various photosurfaces showing their long wavelength response. Boxed symbols refer to the phototube window materials. Excellent rejection ratios and high sensitivity can be seen in the iodine compounds. Curves 1, 2, and 3 are measurements made at GSFC (see text). Curve 4 is from Reference 1; curves 4a and 5 from Reference 6. Curves 6, 7, and 8, shown for further comparison, are taken from Reference 23.

For measurements below the LiF cutoff (1050 Å) it is necessary to use an open window photomultiplier, such as the Bendix magnetic strip multiplier with a tungsten cathode developed by Goodrich and Wiley (Reference 25) and first used by Heroux and Hinteregger (Reference 26) in the late 1950's. Subsequent experiments with this detector have been reported by Hinteregger (Reference 27) and recently by Behring, Neupert, and Nichols (Reference 28) of Goddard Space Flight Center. Current measurements indicate that Cu-I will also prove useful in windowless phototubes as a far ultraviolet photosurface of high quantum efficiency.

## PHOTODETECTOR TECHNIQUES

It should be kept in mind that the spectral response being measured is a combination of the phototube window transmission, the conducting substrate transmission, and the photoemissive response of the cathode material. At the long wavelength end of the response curve, the degree of solar blindness is essentially determined by the amount of cesium or rubidium introduced in excess of the stoichiometric ratio. The greater the excess the more pronounced is the long wavelength tail in the response. A great deal of care must be exercised in tube processing to keep the excess alkali metal

to a minimum (References 9 and 14). The rigid restrictions on the amount of cesium present in a tube rule out, of course, the use of highly cesiated high-gain dynodes. Most frequently used in their place have been dynodes of silver-magnesium (Ag-Mg) or copper-beryllium (Cu-Be).

At the short wavelength end the transmission cutoff characteristic of the phototube window is the principal determinant of the shape of the response curve. Figure 6 is a summary of measurements made during the past year on currently available window and cutoff filter materials. The two curves numbered 5, showing two different sapphire windows, indicate the transmittance variation sometimes found in commercial crystals. The materials represented by curves 7, 8 and 9 are useful in subtractive filter photometry. The other materials are useful as detector windows or as supplementary windows to narrow the photodetector spectral band. Windows of fused silica and sapphire are readily sealed to various glass photodiode and photomultiplier shells by conventional methods, but it is much more difficult to make good seals with windows of cleaved or polished LiF and  $\text{CaF}_2$  crystals. The large expansion coefficients of these crystals have made necessary special sealing techniques—employing silver chloride, silver, and epoxies—which have been only partially described in the literature (References 13, 29, 30, and 31).

At wavelengths greater than 1400Å the slightly lower yield of the photosurfaces shown in these figures might be attributed to a transmittance loss in the conducting substrate. The highly resistive alkali-tellurium and alkali-halide surfaces require that the photoemissive material be deposited on a substrate of some material which is both transparent to the wavelengths of interest and electrically conductive. Very thin deposits (approximately 80 to 90 percent transmittance) of tungsten, nickel, and platinum have proved effective in satisfying both of these requirements.

Figure 7 pictures a variety of photodiodes with sapphire and LiF windows. These diodes are quite small and inherently rugged. The type of ITT diode shown in the figure (second from left) has

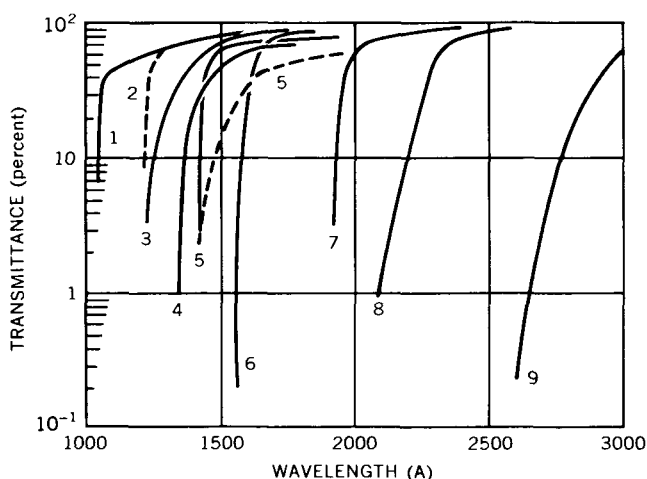


Figure 6—Transmittance characteristics of materials useful in the ultraviolet, uncorrected for surface reflectance: curve 1, LiF (1 mm); curve 2,  $\text{CaF}_2$  (1 mm); curve 3, NaF (1 mm); curve 4,  $\text{BaF}_2$  (1 mm); curve 5, Sapphire (1 mm); curve 6, Fused silica (1 mm); curve 7,  $\text{NiSO}_4 \cdot (\text{H}_2\text{O})_6$  (3 mm); curve 8, Corning 9-54 (7910); curve 9, Corning 9700 (2 mm).

been flown in recent Aerobee-Hi sounding rockets as part of a solar ultraviolet flux photometric experiment. Kretschmar diodes have proved to be very useful in laboratory radiometry. It is important to minimize electrical leakage so that full advantage can be taken of the intrinsically small dark currents from the low thermionic emission of the high work function cathodes described in this paper.

Figure 8 shows some of the photomultipliers mentioned in the previous section. These phototubes have been developed to meet certain requirements for detectors for use in ultraviolet space or laboratory research. These requirements are: (1) suitable cathode sensitivity, (2) suitable solar blindness, (3) suitable windows and window seals, (4) adequate gain and dark current characteristics and, for space environments, (5) ruggedness and small size.

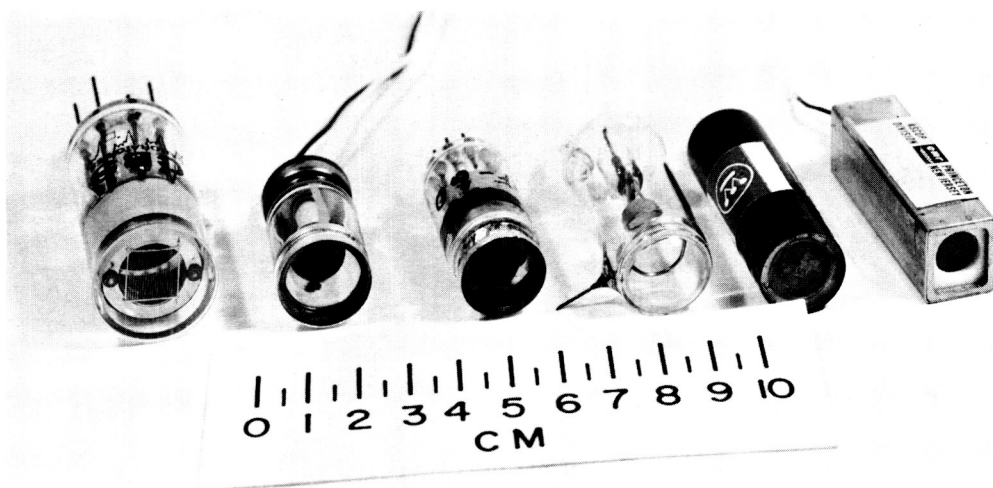


Figure 7—Some of the photodiodes examined at Goddard Space Flight Center. Left to right: CBS CL1051, opaque Cs-Sb cathode, sapphire window; ITT FW156, opaque Cs-Te cathodes, LiF window; RCA, semitransparent Cs-Te cathode, LiF window; Kretschmar, NOLC, opaque Rb-Te cathode, 9741 glass window; Westinghouse, semitransparent Cs-I cathode, LiF window; ASCOP 540F, semitransparent Cs-Te cathode, LiF window.

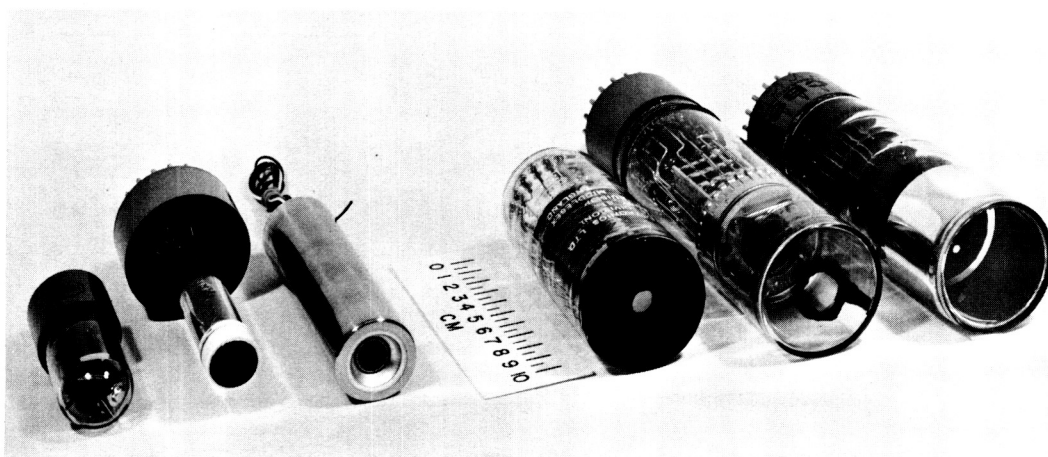


Figure 8—Some of the photomultipliers examined at Goddard Space Flight Center. Left to right: RCA 1P28, Cs-Sb cathode, 9741 glass envelope; RCA C70128 (in test base), semitransparent Cs-Te cathode, LiF window; ASCOP 541F08, semitransparent Cs-Te cathode, LiF window (potted with resistor chain in place); EMI 6256B, semitransparent Cs-Sb cathode, fused silica window; RCA (A. H. Sommer experimental tube), semitransparent Cu-I cathode, LiF window; CBS CL1067, semitransparent Cs-Te cathode, sapphire window.

Relative curves of the distribution of photoelectric quantum efficiencies of the various surfaces were obtained by using a McPherson 1-meter grating monochromator and the double monochromator of the Cary spectrophotometer. The photocathode response is compared with the fluorescence response of sodium salicylate to obtain a relative response curve. Within the accuracy of these measurements the response of sodium salicylate is taken to have a relatively constant quantum efficiency over the wavelength region studied. At wavelengths greater than 3000Å a comparison photocathode, which had

been calibrated against a thermopile, was used as a reference surface. The relative response curves thus obtained were put on an absolute basis by measurements using either a calibrated mercury arc line at 2537A (Reference 32) or a calibrated ion chamber at the 1216A hydrogen Lyman-alpha line. Use was also made of intense lines of other discharges such as the mercury 1849A line.

As a guide for application, the photosurfaces described herein are summarized in Table 1 which shows the wide variety of spectral responses available by combining various windows and cathodes.

Table 1

Typical Photodetector Spectral Response Regions.

The upper figure given for each window material represents typical wavelengths at which the photocathode response is 50 percent of the maximum response; the lower figure, the wavelength at 1 percent of maximum. For cathode materials the spectral region between the short wavelength cutoff and the long wavelength cutoff is a region of  $10^{-2}$  to  $10^{-1}$  photoelectrons/quantum. Some of the values given are averaged from the phototubes reported in this paper. The window cutoff values are taken from Figure 6. The Cs-Sb long wavelength cutoff is estimated from RCA tube handbook data. Those categories for which actual tubes were not yet available were estimated by combining typical window transmittances with typical cathode responses.

Window Materials	Short Wavelength Cutoff (A)	Cathode Materials Long Wavelength Cutoff (A)		
		Cu-I	Cs-Te	Cs-Sb
Glass	3220 3050			4600 7000
Corning 9741	2160 1780		2700 3100	4600 7000
Fused silica	1620 1550	1750 1950	2700 3050	4600 7000
Sapphire	1460 1420	1640 1960	2780 3200	4600 7000
CaF <sub>2</sub>	1300 1220	1420 1880	2700 3100	4600 7000
LiF	1120 1050	1420 1880	2600 2900	4600 7000

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